# CEMENT AND LIME MANUFACTURE

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## Mills for Coarse Grinding.

FROM the earliest days of the grinding industry the normal trend of improvement in grinding mills has been towards a finer product. Originally the jaw crusher, and possibly the roll crusher also, were used in conjunction with mill-stones that became the finishing element. The product obtained was gritty with an amount of fines, the residue on a 16 mesh sieve being probably 15 to 18 per cent., but it is very difficult to obtain exact information of the size and characteristics of the residue that was then normal practice. A less gritty product was obtained later by screening the product and returning the over-size to the mill-stones for further grinding. Later the mill-stones were discarded, and various types of mill having metallic surfaces, in conjunction with screening, became the standard arrangement. These mills gave a product that contained less grit, or a smaller amount of large size particles, but it also contained a reduced quantity of fines or flour.

The product of the earliest compound mill was very gritty; it contained a still smaller quantity of fines and flour, and this proved a serious problem in the development of this type of mill. Subsequently a definite ratio between the mean size of grit and the mean size of the media used for reducing the grit was established, and in taking full advantage of this, and applying the principle to the compound mill, the mill became an economic success. Under some conditions a coarse or gritty product is required, or at any rate a product containing a large amount of fines becomes objectionable, and the purpose of this article is to consider the arrangement and the principal characteristics of two mills that will produce a product of this kind.

As particle size in the product of a mill is a factor of the size of media used in the final stage of the grinding process, it at first appears that a coarser or more gritty product would be obtained with the use of larger media; this is largely true, but the use of large media, under ball or compound mill conditions, invariably

results in, or sets up, a serious increase in the working temperature within the mill, and this causes inefficient grinding and produces a flaky product which is very objectionable.

The number of points of contact with large media is very small compared with the number when small media are used, and in fact there is hardly one point in favour of using large media exclusively for any duty. The only practicable way would be to use a mill of limited capacity, to adopt a large grit-media ratio, to charge the mill with large balls, to operate in conjunction with a separator or classifying cyclone, and to adopt a large circulating feed—say six or eight times the normal feed. This method should remove from the mill all the grit of the desired size as soon as it reaches or even approaches the limiting dimension. Although this appears to be a possible solution the equipment required would be considerable and costly, also the horse-power per ton might be large.

The simplest form of mill most suited for the production of a coarse or gritty product is possibly the plain rod mill or the Rexman rod mill. The former is of the normal tube type and the latter is of the multi-chamber balanced type. Rod media are used in both mills. The former would call for a normal weight of charge and would work at about the same or slightly increased power of mills of the normal type. The latter is of special design and would call for a heavy, or very heavy charge; the mill, however, would work at a very low power, much lower than the usual mills, owing to its balanced construction and method of loading.

The effective length of the tube-type mill would approximate its diameter; it would be fed through one of its trunnion ends and the discharge would be at or through the other trunnion. The length of the rods would be in substantial agreement with the net length of the mill, or there need be only a small amount of end clearance. The diameter of the rods would be from, say, 4in. or 3½in. down to, say, 1½in. or thereabouts in proportionate weights. They would all become smaller as wear took place, the make-up would be generally of the larger size, though some of the intermediate and also the smaller sizes would be required. The charge volume of the rods in this mill would be up to, say, 20 per cent. or even 30 per cent. of the internal volume of the mill; the density of the rod media would be greater than that of ball media or its equivalent. The speed of the mill would be lower than that of the ball or compound mill; a suitable speed would be that obtained by the formula

$$\text{R.P.M.} = \frac{170}{\sqrt{d}}$$

when $d$ is the internal diameter of the mill in inches and the figure 170 is a constant. It will be understood that crushing and grinding in the slower speed rod mill will be effected by the trundling action of the heavy bars or by attrition, and not by impact as in the case of the higher speed ball mill.

*Fig.* 1 gives sections through a rod mill of the usual tube type. The rods would not appear to be packed as closely together as balls of mixed sizes, but as contact obtains for the whole length of the rods the void space is relatively small

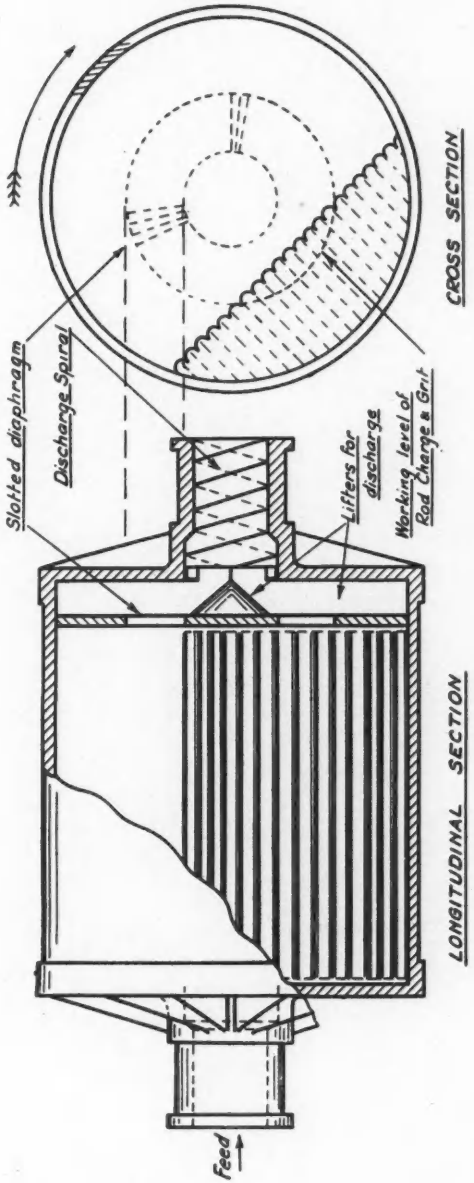


Fig. 1.—Sections through Rod Mill.

—much smaller than is the case with ball media. Ball media weigh up to or about 265 lb. per cubic foot and this, with steel weighing about 480 lb. per cubic foot, gives a void volume of about 44 per cent.; rod media weigh about or up to 325 lb. per cubic foot, and this is equivalent to a void volume of, say, 30 per cent. Assorted sizes of both balls and rods will influence the figures for density or void space.

The resistance to crushing or grinding, the size of feed, and the size of grit that is permissible in the product, would determine the characteristics of the rod material as well as the diameter of the rods, but whatever the characteristics of the material to be ground the material for the rods requires to be both hard

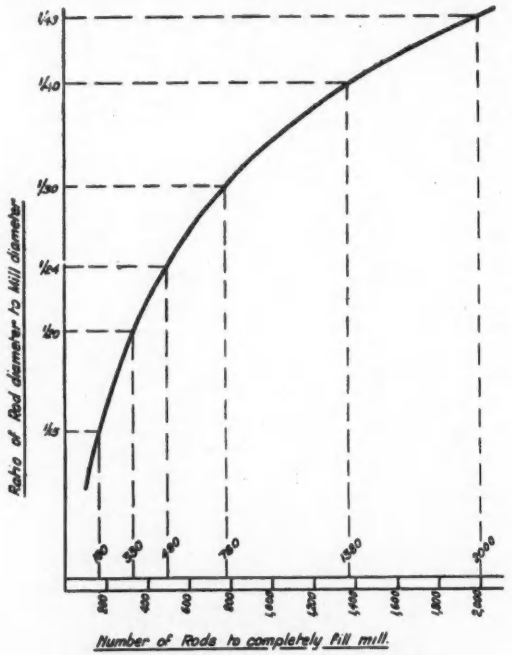


**Fig. 2.—Mills for Coarse Grinding.**

and tough. The rods would probably wear consistently and regularly and there should be little waste; it might be necessary to reverse them—end for end—from time to time to prevent them from becoming tapered or seriously so. Mills of this type, loaded in this way, should be perfectly satisfactory for grinding coal or coke for retort purposes and also for some of the materials now used for fertilisers. The mills would be equally satisfactory for many other purposes where coarse grinding with the minimum of fines is required.

With regard to the number of rods that will be required for mills of any given size, *Fig.* 2 enables this to be ascertained. The left-hand scale indicates the ratio between the bar diameter and the mill diameter. The lower scale indicates

the number of bars that will be required to fill the mill completely ; these numbers would have to be reduced afterwards on a percentage basis to suit the requirement of the charge volume. A typical example will make clear the procedure and the use of the graph.

It is required to find the number of bars required for a 24 to 25 per cent. charge in a mill 5ft. in diameter when the bar sizes range from 3in. to 1½in., the proportion of the different sizes being as given in Table I.

TABLE I.

| Bar diameter (in.) | Weight (lb. per ft.) | Ratio $\frac{d}{D}$ | Percentage and No. of bars | Weight per foot of mill (lb.) |
|---|---|---|---|---|
| 3 | 24·2 | 1/20 | 6% × 330 = 20·0 | 480 |
| 2½ | 16·7 | 1/24 | 6% × 480 = 29·0 | 480 |
| 2 | 10·7 | 1/30 | 6% × 760 = 45·0 | 480 |
| 1½ | 6·0 | 1/40 | 6% × 1380 = 83·0 | 490 |
| | Totals | .. .. | 24% | 1930 |

The formula* upon which the graph is based is

$$N = 0{\cdot}907\left(\frac{D}{d} - 0{\cdot}94\right)^2 + 3{\cdot}7$$

where $N$ = the number of rods, $D$ the diameter of the mill in inches, and $d$ the diameter of the rods in inches ; the other figures are constant. The figures obtained by the formula have been "rounded off" considerably, but even so they should be sufficiently exact for the purpose and as used.

*Fig.* 3 is a longitudinal diagrammatic section through a Rexman rod mill of the balanced type. The mill is supported upon two large diameter bearings and the feed is passed in through one of the trunnions (by means of a feeder tube having an internal spiral, which rotates with the mill) to the centre chamber from which point it is distributed by and between the rods to both ends of the mill, from whence it is discharged through both trunnions.

*Fig.* 4 is a section through the mill and indicates the form of steel castings incorporated in the mill structure and which contain the groups of rod media ; two castings are fitted in each mill. The profile of the mass media is also shown, and a consideration of *Figs.* 3 and 4 show why the mill that carries such a heavy load is able to work at such small power. The rod media used in this mill is usually of nickel-chrome steel as this material alone possesses the characteristics necessary for the duty and the conditions ; bending, as well as wear, make the conditions much more severe than those of the mill referred to earlier.

The diameter and the parallelism of the rods in the Rexman mill to a very large extent determine the grittiness of the product ; the size of the grit in the discharge becomes larger as the amount of wear in the rods increases or as the rods depart from the parallel condition, and owing to this it is necessary to machine the rods parallel when serious wear has taken place. Most wear takes place at about the centre of the length and also at the point at which the rods obtain support in the main castings.

* The formula has been taken from "Machinery Handbook."

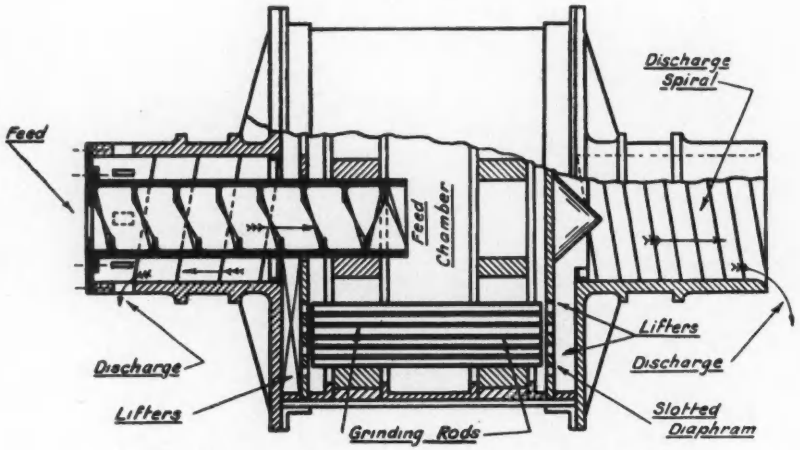


**Fig. 3.—Diagrammatic Section Through Rexman Rod Mill.**

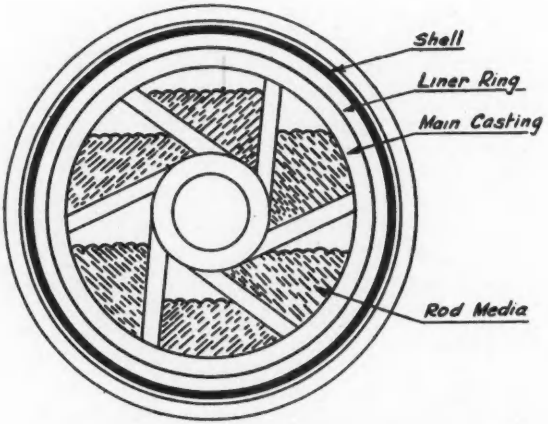


**Fig. 4.—Cross Section of Rexman Rod Mill, Showing Possible Level of Grinding Rods when Mill is at Rest.**

The weight of rods in the Rexman mill would be, say, three or four times the weight of media in a normal mill of comparable size, but the power required for driving the Rexman mill would be only one-third or one-fourth of that required for the normal mill; this is owing to the balanced construction and method of loading. Crushing and grinding in the Rexman mill are effected exclusively by the action of the heavy rods rolling and moving over each other and by the grit passing between the rods as the mill revolves.

The size of rod for the Rexman mill may be determined by the method previously given.

This type of mill appears to be suitable for the hardest material, more especially if it is of crystalline structure. The grittiness of the product, and to a large extent the size of the grit, will be determined by the weight of the separate rods, the parallelism of the rods, and the rate at which feed is passed into the mill. The range of particle size in the product of the Rexman rod mill is usually much more consistent than that of any other mill provided the rods and the rate of feed have the necessary attention.

Either of the mills named would work equally well under either wet or dry conditions provided the constructional details are suitably arranged.

The total number of Rexman rod mills installed in Great Britain is much lower than that of any other kind of mill, but it appears that this mill will serve a useful purpose if the conditions are suitable and the duty is as outlined. The power cost for running it should be very low.

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# The Microscopic Structure of Hydrated Portland Cement.

A PAPER by Mr. L. T. Brownmiller published in the January 1943 number of the *Journal of the American Concrete Institute* gives the results of microscopical examinations of hydrated Portland cements made by the reflected light method commonly used for determining the microstructure of metals and alloys.

The microphotographs, with which the paper is illustrated, demonstrate some additional details of set cements. The first photographs show the rate of hydration of cements up to 28 days, as measured by a decrease in the amount and size of unhydrated particles with age ; they show clearly that the larger particles of the cement are attacked only on the surface by the mixing water, leaving cores in which the principal constituents of the original clinker can be identified readily. These studies gave no evidence that any single major constituent of the clinker was selectively and completely hydrated at 28 days. Other photographs show the relative amount and distribution of the $Ca(OH)_2$ which is formed during the hydration processes. A considerable amount of that compound is formed during the reaction of the cement with water. In the cements examined the amount of $Ca(OH)_2$ is estimated at 10 to 15 per cent. of the total. In the laitance the $Ca(OH)_2$ tends to agglomerate into large crystal aggregates, while within the main body of the cement it is more uniformly distributed in smaller crystals. Other photographs show some structural details of the hydrates other than the $Ca(OH)_2$. The structure of those hydrates is extremely complicated. In general it has been impossible to differentiate them, although in the laitance some relatively large crystals develop, which may be $C_3A$-hydrate.

The method of polishing the hydrated cements was varied from the usual procedure for polishing clinker because of the softer nature of the hydrates, e.g. the $Ca(OH)_2$. The most satisfactory sections were obtained by final polishing by hand on a chamois with tin oxide. Hand-polishing is a laborious procedure, but high-speed wheels tend to tear away the hydrates so that the sections are unsatisfactory. Tin oxide is a more suitable polishing media than ferric oxide since it does not smudge the surface so badly and it is more readily cleaned from the finished specimens.

In general the neat cement specimens used were tough and dense with relatively few voids. Accordingly no impregnants were used in any of the specimens. Usually the hand-polished surfaces were uniform and even with no evidence of loss of hydrates torn away during the polishing process. The specimens were usually mixed with 40 per cent. of water and moulded and sealed in glass vials for 24 hours.

Immediately after removing the specimens from storage a flat surface was ground on them with the finest grade of corundum. The face was stained with several applications of patent blue dye in alcohol. The dye was absorbed by the cement hydrates but not by the unhydrated particles. The dye stain was used primarily to obtain good contrast between hydrated and unhydrated material. After staining, the specimens were allowed to dry for several hours

(or overnight) in an oven at 95 deg. F. to check hydration. The stained surface was then polished on a chamois. Sections which were dried in the oven over night showed no difference from corresponding sections polished immediately after removal from storage. Apparently at 95 deg. F. the surface dries sufficiently to reduce all hydration to a minimum. Specimens prepared in this way may be kept in a desiccator for long periods with no apparent changes in structure. The structure of the hydrated cements depends on conditions of bleeding, laitance formation, amount of storage water accessible to the cement, and other factors. Accordingly in illustrations comparing the rate of hydration of cements at various ages, an attempt was made to photograph fields of each cement at the same position within the specimen. All photographs, except those illustrating laitance formation, were made from fields about 2 in. below the top of the cylindrical specimen and about ¼ in. inside the circumference of the cylinder. In massive concrete where outside water is limited, the conditions of hydration of the cement might be different from those in the small specimens.

Eight photographs were selected to illustrate the rate of reaction of cement with water. After 24 hours the glass vial was broken away and the 3, 7, and 28-day specimens were aged in water. High contrast between hydrated and unhydrated cement was obtained by staining the specimens deeply with the dye and by over-developing the photographic prints. Accordingly the hydrated cement appears black and the unhydrated particles appear white. The specimens were etched for three seconds in a 15 C. solution containing one drop of concentrated HCl in 10 cc. of alcohol. This etchant was used to bring out some of the details of the unhydrated cement, especially the outlines of $C_3S$ and $C_2S$ crystals.

A neat high-early-strength cement after 1-day vial storage contained 66 per cent. $C_3S$, 4 per cent. $C_2S$, and 14 per cent. $C_3A$ by calculation from the oxide analysis. The amount of mixing water was 40 per cent. It is estimated that about one-third of the original cement remained unattacked by the mixing water at one day. The largest particles remaining in the section are about 45 microns in size, and crystals of angular $C_3S$ can be seen in them. The surface area of the cement was 2,580. Particle-size distribution curves showed that about 2 per cent. of the cement was coarser than 60 microns and about 3 per cent. between 50 and 60 microns. The field of the photograph did not show any of the coarsest particles. It is doubtful if any of the 45-micron particles found in the photograph were coarser than 60 microns originally. From the frequency of occurrence of the 45-micron particles in the 1-day hydrate, it is assumed that their average size originally was about 60 microns. If that assumption is correct, then during the first day of hydration the 60-micron particles decreased to 45 microns; that is the radius of the particles decreased 7½ microns during the first day.

A 220 magnification of the same high-early-strength cement at three days (1 day in a vial and 2 days in water) showed that the amount of unhydrated material had decreased to about 5 per cent. Thus hydration had progressed

in accordance with the theories of increased heat of hydration, strength gains, etc. The largest cement particle remaining in this section is about 60 by 30 microns. Undoubtedly that particle was of the 2 per cent. fraction originally coarser than 60 microns. The other larger particles of the photograph are about 30 microns, and it is assumed that the average larger particles have decreased from 45 microns at one day to 30 microns at three days. In other words hydration proceeded into the cement particles at the rate of 7½ microns during the second and third day of water storage.

A similar magnification of the same high-early-strength cement at seven days (one day vial storage and six days in water) showed that practically all of the cement had hydrated, possibly 1 per cent. remaining undecomposed. The larger particles which remain are about 20 microns; it is apparent that these particles have decreased from 30 microns at three days to about 20 microns at seven days. Thus hydration has advanced 5 microns into the particles from three to seven days. During the first seven days the rate of hydration along the radius of the particles of this particular cement may be estimated as follows: 1st day, 7½ microns; 2nd and 3rd days, 7½ microns; 4th to 7th days, 5 microns. The rate of hydration of the particles of this particular cement proceeded into the individual grains at the rate of 20 microns during the first seven days. During that period particles which were originally finer than 40 microns were probably completely hydrated, while 60-micron particles may still be 20 microns in size at seven days.

Another field of the 7-day hydrate of the high-early-strength cement at 220 magnification shows that a small amount of oversize material was present in the cement. One coarse particle, about 70 by 90 microns after 7-days' hydration, is visible in this field; crystals of angular $C_3S$ are plainly visible. Except for one particle, the general appearance of the 7-day hydrate is about the same as that of the previous specimen.

Thus in a finely-ground cement of high $C_3S$ and high $C_3A$ content there is very little unhydrated material left after 7-days' storage to give substantial increases in strength by continued hydration. Kühl described this hydraulic hardening of cements as a process in which "the inner, deep layers of cement grains are sucking off water from the hydrogel, which process is accompanied by a hydration of these layers. Gel which is on the surface of a grain envelops it more and more closely until it reaches complete water-tightness." These illustrations seem to confirm his conception of hydraulic hardening.

Other photographs show similar progressive hydration of a cement of 1,800 surface area. The calculated composition of the cement showed 48 per cent. $C_3S$, 24 per cent. $C_2S$, and 12 per cent. $C_3A$. This cement had a 7 per cent. residue on the 200-mesh sieve. No attempt is made to estimate the rate of hydration of this cement because the size distribution curves gave no narrow classification of the particles coarser than 60 microns on which to base such calculations.

Specimens of 3-day hydrate with a lower surface area than those previously described contained a larger amount of coarse material which is plainly visible

by a comparison of the photographs. Approximately 25 per cent. of the cement remained unhydrated at three days; in the 3-day high-early-strength cement about 5 per cent. remained. The largest unhydrated particle remaining in this cement at three days is about 75 microns in size. In the 7-day hydrate of the same cement there is a noticeable decrease in the amount of unhydrated material remaining as compared with the 3-day hydrate. Less than 20 per cent. remained unhydrated at seven days. The largest particle in the 7-day hydrate is approximately 60 microns, in which one well-developed hexagonal crystal of $C_3S$ is visible. Two round crystals of $C_2S$ can be seen in the particle, illustrating clearly the difference in crystal habit of the two silicates. $C_3S$ generally develops with straight-line edges and angles while $C_2S$ usually assumes a rounded form. Under favourable conditions of crystallisation $C_3S$ often develops the hexagonal form.

In the 28-day hydrate of the same cement there is not much difference in the amount of unhydrated material as compared with the 7-day hydrate. The amount remaining in the 28-day hydrate is estimated at about 15 per cent. The largest particle of unhydrated cement in the 28-day hydrate is triangular in shape and 70 by 100 microns. The rounded forms of $C_2S$ can be seen in it. $C_3S$ can be identified in one particle.

The illustrations show that as mortars age in water there is progressive hydration of the cement particles. The smaller particles are hydrated first while the larger particles gradually decrease in size but may only be completely hydrated after years of exposure. The illustrations show that in a cement which is not too finely ground there is still unhydrated material remaining after 28 days to continue the hydration and hardening processes by withdrawing water from the gel to seal it more firmly and to make it more watertight.

In a section taken from a concrete road after six years' exposure (440 magnification) a particle of unhydrated cement about 70 microns can be seen. Angular crystals of $C_3S$ and rounded $C_2S$ can be distinguished in it. Some grains of sand are visible embedded in the hydrate.

The remaining photographs of the paper were made from neat cement specimens stored in sealed glass vials until the time of examination. No water other than the mixing water was in contact with the specimens at any time. These specimens were only lightly stained with patent blue, and the photographic prints were not over-developed so that the contrast between hydrated material and unhydrated particles is not accentuated. Accordingly the cement hydrate appears medium grey instead of black, while the unattacked particles are light grey or white.

Two photographs illustrate the size distribution of particles of a Type 2 cement as affected by laitance formation and bleeding. These photographs, at 220 magnification, were taken along a vertical plane in the cylindrical specimen. In the laitance the size and the number of unhydrated grains increases with the depth from the top. Below the layer of laitance the coarser unhydrated particles typical of the cement are present. The laitance contains a higher percentage of hydrated material than is present within the body of the section.

Two photographs were taken in planes parallel to the top of the specimen. One, taken about $\frac{1}{64}$ in. below the top of the cylinder at 450 magnification, represents the laitance and shows only a small amount of very fine unhydrated material. Practically the entire substance of the laitance is composed of medium grey hydrates. The other, taken 2 in. below the surface of the same specimen, shows numerous unhydrated particles of varying size embedded in the medium grey hydrate. The section was etched in the acid etchant and outlines of $C_3S$ and $C_2S$ crystals can be seen in the larger particles. A 30-micron particle shows distinctly angular crystals of $C_3S$ embedded in interstitial matter; some partly-decomposed $C_3S$ crystals are visible along the outer edge of the particle. The interstitial matter consists largely of calcium aluminates and ferrites or their combinations such as $C_4AF$, "glass," etc. A 10-micron crystal of round $C_2S$ has a thin layer of interstitial matter enclosing it. In a group of $C_2S$ crystals hydration has proceeded as far as the boundaries of some of the crystals but does not seem to have attacked them noticeably.

In an unetched section of the 28-day hydrate of Type 2 cement at 450 magnification there is a 70-micron cement particle showing round $C_2S$ crystals embedded in the lighter interstitial matter. A crystal of partially-hydrated hexagonal $C_3S$ also lies within the group. The hydrated portion of the $C_3S$ is darker than the unhydrated part, but still retains the angular shape of the original crystal. The hydrate was moulded and confined to that shape by the shell of interstitial matter which apparently has not yet been attacked by the water. In the same group another completely hydrated crystal of $C_3S$, identified by its straight-line edges, has merged entirely with the surrounding hydrate at one end where the confining shell of interstitial matter has been broken.

In another field of the 28-day hydrate of Type 2 cement at still higher magnification (900) there is an irregular elongated cement particle approximately 70 microns long. It consists of medium grey $C_3S$ and white interstitial matter. Originally when the cement was mixed with water this particle was attacked by the water from all sides to form the dark grey hydrate around it. At 28 days the reaction advanced to an irregular edge limiting the unhydrated particle. Those portions of the $C_3S$ crystals which have been hydrated have lost their form and have merged with other hydrates to form a compact mass around the grain. From the photograph it is evident that the $C_3S$ has hydrated faster than the interstitial matter which protrudes beyond those crystals and into the hydrate. Two semicircular outlines can be seen limiting the unhydrated particle. These areas were probably occupied by round $C_2S$ crystals originally; at one point hydration has been complete, but there remains a narrow saw-toothed skeleton of unhydrated $C_2S$ along the edge.

These photographs show that the unhydrated material remaining in at 28 days consists of $C_3S$, $C_2S$, and interstitial matter, which are the three principal constituents of the clinker. These constituents undoubtedly react at different rates if all are in contact with water. But particles are often composed of large aggregates of crystals which must be decomposed from the outside before the

centres can react. Accordingly no single major constituent of cement is entirely and selectively decomposed at any age. These examinations gave no evidence of channelling of the water into the grains to hydrate the more reactive $C_3S$ which might lie in the centre of a particle. Hydration seems to proceed by the gradual reduction in the size of the particle as a function of the surface exposed to the water. Small crystals of $C_2S$ may hydrate long before the decomposition of large $C_3S$ crystals is complete. No attempt was made to differentiate interstitial matter into its various constituents.

In a 7-day hydrate of Type 1 cement at 450 magnification the light unhydrated cement particles can be distinguished readily from the darker grey hydrates. The two largest unhydrated particles are about 100 microns in size. This cement shows the presence of periclase magnesia, which can be recognised readily by the distinctly black outlines typical of those crystals. They are present in both the hydrated and unhydrated cement. Delayed expansion of cement is often attributed to the hydration of the MgO to $Mg(OH)_2$, which is accompanied by an increase in volume, setting up stresses in the cement.

In an unetched section of a 28-day hydrate of Type 1 cement at 900 magnification is an unhydrated cement particle containing some very small crystals of MgO. Other crystals of MgO are embedded in the darker hydrate. One of the crystals of MgO shows the typical hexagonal form of periclase ; it is about 7 microns in size. Close inspection of the edge of this crystal shows some pitting, probably due to slight hydration. As it continues to hydrate there will be an increase in volume ; it is doubtful, however, if a single crystal of this size would set up stresses sufficient to disrupt the cement.

A further series of photographs illustrates some of the structural details of the hydrate.

A Type 2 cement hydrate stored in a glass vial for 28 days contained 40 per cent. $C_3S$, 31 per cent. $C_2S$, 6 per cent. $C_3A$, and 13 per cent. $C_4AF$. The section was etched in water at 15 deg. C. for one second. The water etched the $Ca(OH)_2$ of the set cement, which appears as the finely crystalline, black constituent distributed throughout the section. A considerable amount of $Ca(OH)_2$ is liberated when cement hydrates ; the amount of $Ca(OH)_2$ is estimated at 10 to 15 per cent. The crystals are present throughout the mass of hydrogel and are often present in groups or agglomerates. In one photograph concentrations of $Ca(OH)_2$ are more plainly evident at a magnification of 440. The photographs show clearly that structurally the laitance is different from the body of the cement.

# Phase Equilibrium Studies involving Potash Compounds in Portland Cement.

A FURTHER report has been published on the research work by Mr. William C. Taylor, of the United States National Bureau of Standards, on " Phase-Equilibrium Studies Involving the Potash Compounds of Portland Cement, and is published in the Bureau's *Journal of Research* for December, 1942. A summary of the previous report was given in this journal for March and April, 1942. This research on the system $K_2O.23CaO.12SiO_2$-CaO-$5CaO.3Al_2O_3$ is a part of a programme designed to determine the manner in which $K_2O$ affects the compound composition of Portland cement clinker. The only compounds that were observed in the system under equilibrium conditions are the components of the system and $3CaO.Al_2O_3$. The effect of $K_2O$ on the compound composition of clinker containing $K_2O$, CaO, MgO, $Al_2O_3$, $Fe_2O_3$, $SiO_2$, and $SO_3$ has been studied also. The only compounds of $K_2O$ found to be stable are $K_2SO_4$ and $K_2O.23CaO.12SiO_2$, the $K_2O$ combining preferentially with the $SO_3$ present.

An introduction to the report states that the compositions and the amounts of the various compounds in Portland cement clinker are determined by the relations of the several oxides to one another during the thermal treatment given the raw mixture. Because of the complications attending studies of system containing more than three components, the most convenient approach to relations of the oxides to each other consists in a series of investigations of binary and of ternary systems. The most advantageous course of study to be followed in this step-by-step process may be indicated by examining the products of reactions between an established clinker compound and an additional oxide or a newly-established compound.

This procedure is being followed in determining the relation of the component $K_2O$ to the other oxide components of clinker. Brownmiller found that $K_2O.Al_2O_3$ is the only compound of $K_2O$ that will crystallise from the melt in all portions of the $K_2O$-CaO-$Al_2O_3$ system studied. The present author found that $K_2O.Al_2O_3$ and $4CaO.Al_2O_3.Fe_2O_3$ form a binary system with one eutectic, no additional compounds being formed. In the same study, it was shown that for a given ratio of $4CaO.Al_2O_3Fe_2O_3$ to $2CaO.Fe_2O_3$, the solid solution of these two compounds and $K_2O.Al_2O_3$ form a pseudo-binary system with a definite lowest-melting composition. In the study that followed, it was found that $K_2O.Al_2O_3$ reacts with $2CaO.SiO_2$ and with $3CaO.SiO_2$ to form a potash-lime-silica compound This compound was later shown in the study of the system $K_2O.CaO.SiO_2$-$2CaO.SiO_2$ to have the composition $K_2O.23CaO.12SiO_2$. Examination of the products of reactions involving $3CaO.Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$, and $K_2O.23CaO.12SiO_2$ revealed that $K_2O.23CaO.12SiO_2$ exists in a region of the $K_2O$-CaO-$Al_2O_3$-$Fe_2O_3$-$SiO_2$ system in which Portland cement compositions fall.

The present investigation of the system $K_2O.23CaO.12SiO_2$-CaO-$5CaO.3Al_2O_3$ was undertaken for the purpose of establishing the existence or non-existence of other compounds of potash in the system and of determining the fields of

stability of the various compounds formed when mixtures of $K_2O$, CaO, $AlO_3$, and $SiO_2$ comparable with Portland cement clinker compositions are heated.

Since $SO_3$ and MgO are components of almost every commercial clinker, the effects of these oxides on the manner in which $K_2O$ is combined in clinker were studied, and the results are included in this report.

## Experimental Method.

The compounds forming the components of the system $K_2O.23CaO.12SiO_2$-$CaO$-$5CaO.3Al_2O_3$ were prepared first and the exact composition determined by chemical analyses and microscopical examinations. This preparation of $5CaO.3Al_2O_3$ was found to melt sharply at a temperature between 1,454 deg. and 1,458 deg. C. as measured by means of a calibrated thermocouple. Rankin and Wright give 1,455 deg. $\pm$ 5 deg. C. as the melting point of this compound.

Each of the compounds was heated to about 1,250 deg. C. for half an hour immediately before the proportioning of the various mixtures. The mixtures then were intimately ground in an agate mortar. Small charges for thermal study were taken from these base samples, the general procedure previously outlined being followed. Similar methods were employed in the study of other high-temperature reactions.

The following notes are taken from the report.

Previous studies have shown that there is no reaction between $K_2O.23CaO.12SiO_2$ and CaO, in the sense that no additional crystalline compound is formed. The liquidus temperatures in this system are beyond the limits of the equipment in use (about 1,600 deg. C.), and therefore the boundary curve is undetermined. Extrapolation of the boundary curve between the fields of $K_2O.23CaO.12SiO_2$ and CaO in the ternary system indicates that a simple eutectic may consist of about 85 per cent. of $K_2O.23CaO.12SiO_2$ and 15 per cent. of CaO.

The system $CaO$-$5CaO.3Al_2O_3$ is a portion of the more inclusive system $CaO$-$Al_2O_3$, reported in detail by Rankin and Wright.

No intermediate compound is formed in the system $K_2O.23CaO.12SiO_2$-$5CaO.3Al_2O_3$. The eutectic, melting at 1,330 deg. $\pm$ 5 deg. C., consists of 21·5 per cent. of $K_2O.23CaO.12SiO_2$ and 78·5 per cent. of $5CaO.3Al_2O_3$ (oxide composition: $K_2O$, 0·96 per cent.; CaO, 50·68 per cent.; $Al_2O_3$, 41 per cent.; $SiO_2$, 7·36 per cent.). In the binary system $K_2O.23CaO.12SiO_2$-$5CaO.3Al_2O_3$, and in the ternary system $K_2O.23CaO.12SiO_2$-$CaO$-$5CaO.3Al_2O_3$ no evidence of solid solution of $K_2O$ in $5CaO.3Al_2O_3$ was obtained, no deviation from the value 1·608 as the index of $5CaO.3Al_2O_3$ being obtained in any case.

No new compounds exist in equilibrium with the liquid in the ternary system. The products of final crystallisation are the components of the system and $3CaO.Al_2O_3$.

## Potassium Sulphate in Commercial Clinker.

In addition to the data obtained in this investigation, other workers have obtained results which indicate that $K_2SO_4$ is likely to be found in commercial clinker. In 1936, L. S. Brown observed in dust taken between a kiln coating and the underlying brick, and subsequently in clinker, a low-index phase that was tentatively identified as an alkali sulphate. Kalousek, Jumper, and Tre-

goning report that a correlation exists between the amounts of water-extractable $K_2O$ and the amounts of the available $SO_3$ in the clinker, which indicates that $K_2O$ is present in many clinkers partly as $K_2SO_4$. Woods, in a study of the volatilisation of alkalies from two clinker raw mixtures during calcination, observed that the addition of $CaSO_4$ to the mixtures inhibits the voltatilisation of potash.

The correlationship was examined between the $K_2O$ and $SO_3$ contents of 26 commercial clinkers together with portions of them which had been slowly and quickly cooled after reheating to clinkering temperatures. In general, there was an increase in the $K_2O$ content as the amount of $SO_3$ increased, indicating that generally the amount of potash in a clinker is in excess of that required for the formation of $K_2SO_4$ from the $SO_3$ available. Nineteen of the clinkers were examined by the petrographic microscope for $K_2SO_4$ crystals. Potassium sulphate was identified in 11 of them. This compound was observed in all but two instances in which the calculated potential $K_2SO_4$ was over 0·24 per cent. and in no case where the calculated $K_2SO_4$ fell below that value.

**Effect of MgO on the constitution of Clinker containing $K_2O$.**

Ward, in his comparisons between the calculated and microscopically observed phases of commercial clinker, reports that the agreement between the values for free MgO as determined microscopically and as calculated was usually good. This indicates that the stability of MgO is not affected by the existence of the potash compounds in clinker. In order to obtain direct evidence of this nature, a mixture containing 99 per cent. of $KC_{23}S_{12}$ and 1 per cent. of MgO was prepared and a sample heated at 1,525 deg. C. for one hour. The resulting charge showed no evidence of melting and, upon examination, was found to consist of only two phases: $K_2O.23CaO.12SiO_2$ and periclase (MgO).

A second mixture containing 99 per cent. of $K_2SO_4$ and 1 per cent. of MgO was also prepared. A charge was heated at 1,400 deg. C. for one hour. A microscopical examination revealed no evidence of interaction of the $K_2SO_4$ and MgO.

## Summary.

The only crystalline phase other than the components observed in the system $K_2O.23CaO.12SiO_2$-CaO-$5CaO.3Al_2O_3$ under equilibrium conditions was the compound $3CaO.-Al_2O_3$ normal in crystalline form and optical properties. No evidence of any high-temperature modifications of any of the compounds of the system was obtained.

When both $SO_3$ and $K_2O$ are components of clinker it was found that $K_2O$ combines preferentially with $SO_3$ to form $K_2SO_4$. In mixtures of $K_2O$, CaO, $Al_2O_3$, $FeO_3$, $SiO_2$, and $SO_3$ in proportions comparable with those in Portland cement clinker, any $K_2O$ in excess of that required for the formation of $K_2SO_4$ combines with CaO and $SiO_2$ to form $K_2O.23CaO.12SiO_2$, provided crystallisation occurs under equilibrium conditions. Potassium sulphate has been identified in several commercial clinkers.

No reaction of either $K_2SO_4$ or $K_2O.23CaO.12SiO_2$ with MgO has been observed, which indicates that the presence of MgO does not affect the manner in which $K_2O$ is combined in clinker.